

**THE USE OF SIMPLE RAPID COLORIMETRIC TECHNIQUES FOR  
MEASUREMENT OF LIGHT CYCLE OIL CONTENT AND  
RELATIVE STORAGE STABILITY OF DISTILLATE FUELS**

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**ABSTRACT** A simple colorimetric technique has been developed which accurately measures the relative amount of unhydrogenated light cycle oil in distillate fuels. Distinctive colours are formed within 10 minutes from the addition of 1 - 2 ml of fuel to a small column of active white powder in clear glass or plastic tubes. Visually, the intensity and colouration of the powder may be immediately correlated with the type and amount of light cycle oil in the fuel. Analytical values with higher degrees of precision for light cycle oil contents in the 0 to 30% range are obtained by washing the coloured material from the tubes with solvent and measuring the absorbance with a colorimeter or spectrophotometer. Results are presented for the correlation between colorimetric values, unhydrogenated light cycle oil content and diesel fuel storage stability.

**INTRODUCTION**

Many studies have implicated polar compounds of oxygen,<sup>1,2</sup> nitrogen<sup>3</sup> and sulphur<sup>4</sup> in hydrocarbon fuel mixtures for the degradation of hydrocarbon fuels upon storage. However, although many mechanisms have been postulated, none of these processes will fully explain the nature of the sediment formed by degradation of automotive diesel fuel.<sup>5</sup>

Better understanding of the chemistry of diesel fuel degradation will not only allow development of rapid and accurate tests for the measurement of fuel instability, but also modification of refinery processes to minimize the formation of detrimental species. The presence of unhydrogenated middle distillate light cycle oil from cracking of heavier petroleum components plays a significant role in the degradation of automotive diesel fuel.<sup>6</sup>

Rates of possible processes occurring in automotive diesel fuel containing light cycle oil have been investigated towards understanding the chemistry of fuel degradation.<sup>7</sup> Variations in absorbance in both the ultraviolet and visible regions were used to measure rates of reaction.<sup>8</sup> The colour of species which absorb in the visible region of the spectrum can be detected by eye. In this paper, the use of visual and instrumental absorption procedures are presented to illustrate the ease with which light cycle oil can be detected by direct means in as little as 0.5 ml of automotive diesel fuel.

**EXPERIMENTAL**

Reference fuels used in this study were samples from automotive distillate refinery streams of straight run distillate (SRD), light cycle oil (LCO) and hydrotreated light cycle oil (HTLCO) obtained directly from Australian refineries within one week of production. Samples were either blended immediately for ageing studies or stored as unblended components at -12°C. Experimental blends were prepared by mixing on a volumetric basis freshly thawed

LCO or HTLCO with SRD. Ten commercial automotive diesel fuels purchased directly from retail outlets were also included in this study.

The LCO Colorimetric Tubes were prototype units developed at the Materials Research Laboratory of the Defence Science and Technology Organization. Results obtained in this study were obtained with 4 cm of active white powdered solid material packed in 5 mm diameter glass tubes. It is anticipated that standardized Colorimetric Tubes will be produced commercially in unbreakable clear plastic packs under licence to the Commonwealth of Australia.

Plastic syringes were used to add 2 ml of fuel to the Colorimetric Tubes and apply gentle pressure so that the fuel passed through the column of powdered material in the tubes within 30 seconds. Colour development commenced immediately on the white powder and in most cases full visual development was achieved at ambient temperatures within 10 minutes. Spectral measurements reported in this paper were obtained after washing the column with 1 ml of hexane to remove residual fuel followed by 6 ml of methanol. In each case, gentle pressure was applied from the syringe used to add the liquid so that it passed through the powdered solid within 30 seconds. Spectra were recorded immediately in the methanol wash liquid using 1 cm pathlength cells.

Comparative ageing studies were done at 43°C for 13 weeks by the method of ASTM D4625 or by an oxygen overpressure technique at 90°C.<sup>9</sup> The single bomb apparatus of ASTM D942 was used for the oxygen overpressure measurements as described elsewhere.<sup>10</sup>

## RESULTS AND DISCUSSIONS

Results reported in this presentation represent colorimetric development which was the composite of a large number of chemical processes from which possible reactions may be postulated.<sup>8</sup> The active solid powder was a mixture of a number of possible ingredients which may be formulated with a large range of activities and selectivities. The white powder acts both as an active catalyst and solid support for colour development.

Visual colour development was rapid (within 5 minutes) and occurred in contact with very small amounts of unhydrogenated LCO. One batch of active powder had to be discarded after being coloured by accidental contact with a stirring rod which was unwashed after being used to stir a blend of LCO. The normal human eye is very sensitive to differentiating comparative shades of colour which are difficult to reproduce in coloured photography and not feasible in a black and white conference proceedings. Maximum selectivity to visual observations for a range of LCO concentrations was obtained by using an active powder with low catalytic activity. Coloured slides of Colorimetric Tubes forming part of the in-session presentation are from tubes with low catalytic activity.

Medium to high catalytic activity promotes more rapid colour development (no further noticeable visual changes after one minute) and a final colour which was black or a very dark blue/green. The visual colour variation was greatly reduced for a range of LCO from 0 to 30%. However, if coloured material was washed from the active powder as described in the experimental section, a variation in the absorbance was readily seen as determined by a simple colorimeter or a spectrophotometer.

The rapidity of the colour development is shown in Figure 1, in which the Colorimetric Tubes of medium catalytic activity were washed after 2 to 1500 minutes following the addition of 2 ml of fuel containing 15% LCO oil from refinery F (refinery designations as in other presentations at this conference<sup>11</sup>). Both the absorbance and the peak maximum were a function of time. However, from 300 to 1400 minutes the absorbance at 650 nm was relatively constant. This follows from the broad band absorbance in the region 600 - 700 nm which is

shown in Figure 2 for the fuel after 300 minutes contact time with the active powder in the Colorimetric Tube.

Following from Figures 1 and 2, it was concluded that the most consistent results would be obtained by allowing fuel material to stand on the Colorimetric Tubes for 16 hours (overnight) at ambient temperatures. After the coloured material was washed from the tubes, the absorbance was recorded at the maximum in the region 600 - 700 nm.

Results obtained with 5 blends of LCO from three refineries are shown in Figure 3. The variation of the absorbance with concentration was approximately linear from 0 to 30% LCO content. Refineries A and G were processing Australian Bass Strait crude at the time the samples were obtained, whereas refinery F was processing Middle Eastern crude. It may be noted that the absorbance for a constant LCO content from refinery F was approximately twice that from refineries A and G. It was of interest to compare the amount of sediment produced both by ASTM D4625 and oxygen overpressure ageing as shown in Table 1.

FUEL SAMPLE	ASTM D4625 mg/L	OXYGEN OVERPRESSURE mg/L
A	18	8
F	15	33
G	12	11

**Table 1.** Sediment produced by ageing 30% LCO in the SRD for 13 weeks at 43°C under ASTM D4625 conditions or 16 hours at 90°C under 794 kPa oxygen overpressure conditions.

Fuel from refinery F which produces the greatest absorbance from the Colorimetric Tubes, produces the most sediment from the oxygen overpressure ageing, but not from the 43°C ageing. The absorbance produced by the fuel mixtures from refineries A and G was very similar, whereas there was a small variation in the amount of sediments produced by the two ageing procedures.

Whereas approximately linear correlation was obtained between the amount of absorbance from Colorimetric Tubes and light cycle oil content (Figure 3), the amount of insoluble sediment produced by increasing LCO content was not linear as shown in Table 2.

It was most probable that chemical reactions producing soluble precursors to insoluble particulate matter increase with increasing LCO content. LCO has a much higher aromatic content (50-80%) than SRD (10-20%) and is a much better solvent than SRD for the insoluble particulate matter. Thus less insoluble matter precipitates from solution. However, the particulate precursors remain in solution where they have an increased tendency to form injector and possibly cylinder deposits. Thus for measurement of LCO content and possible injector deposit potential, the Colorimetric Tubes offer higher precision than gravimetric measurements of deposit formation on ageing.

LCO %	TOTAL SEDIMENT mg/L
5	11
10	20
15	28
20	29
30	33

**Table 2.** Sediment produced by ageing LCO/SRD blends from refinery F under oxygen overpressure conditions of 794 kPa oxygen at 90°C for 16 hours.

A number of Australian retail automotive diesel fuels have been tested with the Colorimetric Tubes. The absorbance produced after passing 10 retail fuels through Colorimetric Tubes of low activity is shown in Figure 4. Reference fuels are 0 and 1% LCO from refinery G and 5% LCO from refineries A and G. Low activity tubes were used so that visual selection of LCO content could be compared with that obtained by absorbance measurements. As may be seen from the coloured slide projection prepared for oral presentation of this paper, visually fuel 2 is readily selected as producing the darkest blue/green colouration, comparable to that produced by the 5% LCO standards. Fuels 3, 7 and 6 follow in colour intensity of the tubes. Fuel 9 was readily selected as having the least blue/green colour development of the Colorimetric Tubes.

Fuels 2 and 9 were subject to oxygen overpressure ageing at 794 kPa pressure for 64 hours at 95°C. Although this accelerated ageing might be compared to 3-5 years ambient ageing,<sup>9</sup> only 12 and 1 mg/L of insoluble sediment was produced, consistent with the low and very low levels of unhydrogenated LCO respectively in the fuels.

Undiluted hydrotreated LCO was also passed through the Colorimetric Tubes. That from refineries C and D (reference 10) produced very little colour development, whereas that from refineries E and F produced medium and intense colour development respectively. These results are comparable with sediment levels from 13 weeks 43°C ageing of 30% hydrotreated LCO/SRD blends of less than 1 mg/L from refineries C and D and 8 and 19 mg/L from refineries E and F. It was concluded that either the hydrotreatment process producing the sample at refinery F was ineffective or the sample was unrepresentative.

## CONCLUSIONS

Colorimetric tubes have been shown to be a rapid and simple means of determining the amount of unhydrogenated LCO middle distillate fuels either by direct visual means or more quantitatively by colorimetric or spectrophotometric measurements. They are non-toxic and relatively inexpensive to produce and may be used by non-technical personnel in a field environment to obtain direct measurements of relative unhydrogenated light cycle oil content of hydrocarbon fuels. With 2 ml of fuel or less, measurements may be obtained within 10 minutes.

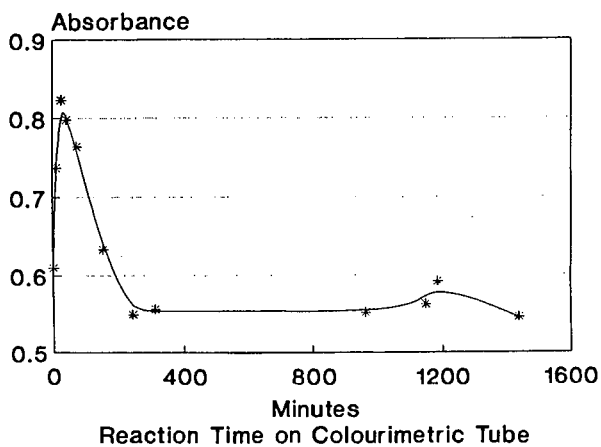
The colour formation on the tubes has been shown to be proportional to both the type of unhydrogenated LCO and the amount in a fuel. The amount and type of LCO may then be

correlated with the formation of sediments by ambient or accelerated ageing techniques. The rapidity and simplicity of the technique makes it ideal for use as a quality control technique at all points of the distribution system, from the refinery outlet, bulk distribution terminal through to the consumer holding tanks. They may be used with any fuel for which control of unhydrogenated LCO is considered desirable. This is primarily the higher quality diesel fuel market at the moment, but the sensitivity of the technique lends itself to determining the effectiveness of hydrogenation for hydrogenated LCO added to aviation distillate.

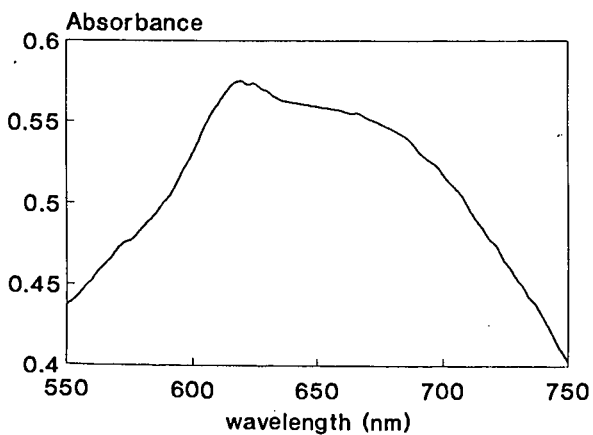
The Colorimetric Tubes accelerate the rate of reactions of species associated with LCO in small amounts of fuel and concentrate the products in a form which is readily measured. Their use with a wide range of fuels has much potential to enable comparison of the species present in the fuels and a wider understanding of the chemistry associated with fuel instability.

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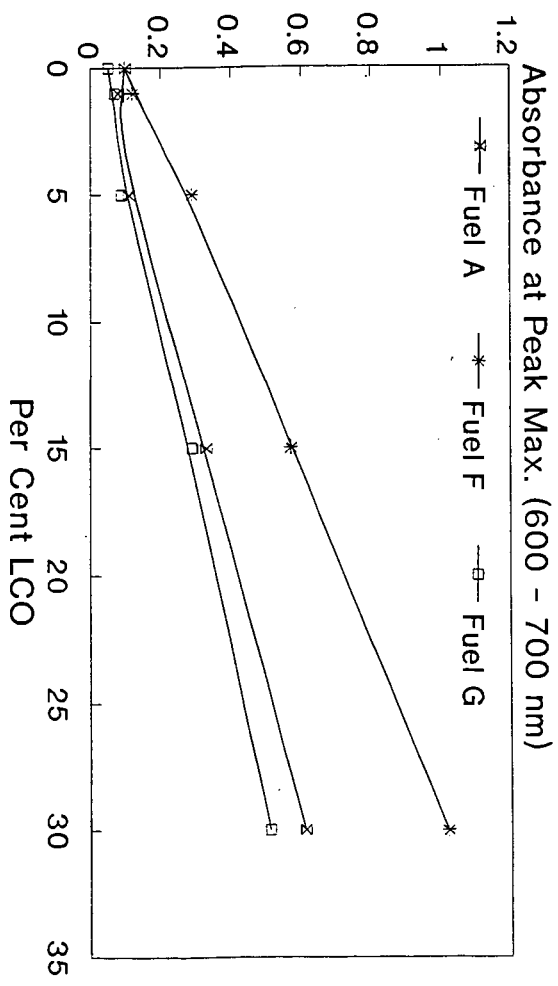
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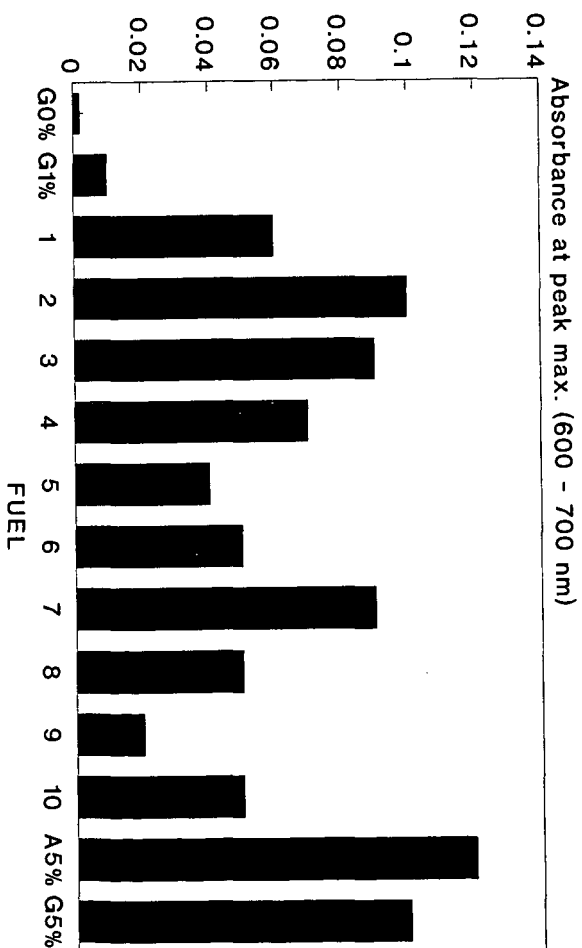
**Figure 1.** Variation of absorbance at 650 nm of Colorimetric Tube methanol washings for 15% LCO/SRD mixtures of Fuel F.



**Figure 2.** Spectra of Colorimetric Tube methanol washing after 300 minutes reaction time on tube for Fuel F.



**Figure 3.** Absorbance of medium activity Colorimetric Tube methanol washings after 16 hours reaction time on the tube at ambient temperatures for Fuels A, F and G.



**Figure 4.** Absorbance of low activity Colorimetric Tube methanol washings after 16 hours reaction time on the tube for 10 commercial automotive diesel fuels compared to 0, 1 and 5% LCO/SRD standards for Fuels A and G.